AMENDED SHEET

AQUEOUS COLLOIDAL SUSPENSION OF THE HYDROXIDE OF AT LEAST ONE TRANSITION ELEMENT, FOR THE PURPOSE OF THE REDUCTION OF CHROMIUM IN CEMENT

The invention relates to an aqueous colloidal suspension of the hydroxide of at least one transition element and/or of tin whose oxidation-reduction potential is less than that of the $CrO_4^{2-}/Cr(OH)_3$ couple (-0.12 V) with a pH between 2 and 11, limits excluded, and containing less than 0.02% of soluble ions of at least one transition element and/or of tin in solution, the suspension being designed to reduce the chromium VI content of cement to a value at most equal to 2 ppm.

The invention more particularly relates to an aqueous suspension of tin hydroxide with an oxidation-reduction potential of -0.96 V, of iron hydroxide with an oxidation-reduction potential of -0.56 V, of manganese hydroxide with an oxidation-reduction potential of -0.4 V, implemented alone or as a mixture, with a pH between 2 and 11, limits excluded, designed to reduce the chromium VI content of cement to a value at most equal to 2 ppm, the suspension being stabilised by means of a stabilisation agent.

The invention also relates to the use of aqueous suspensions of tin hydroxide, and/or iron hydroxide and/or manganese hydroxide of pH between 2 and 11, limits excluded, designed to reduce the chromium VI content of cement during the process of preparation of the cement to form a treated cement whose chromium VI content has a value at most equal to 2 ppm.

The invention finally relates to a process for treatment of cements to reduce the chromium VI content of the cement to a value at most equal to 2 ppm.

It is known that cements contain chromium compounds which, when the cements are mixed with water, appear in the form of chromium VI dissolved in water. Now, chromium VI soluble in the water of the cements may be the origin of allergic reactions for persons who come in contact with products containing hydrosoluble compounds of hexavalent chromium. Chromium is even suspected of being carcinogenic for the human. Thus, construction workers whose skin, in general the hands and the arms, is brought in regular contact with mixtures of cement and water are capable of contracting contact eczema due to the too-elevated chromium VI content of the cements.

Systems exist in the state of the art that are designed to reduce hydrosoluble hexavalent chromium compounds in the cements. It is known for example that the addition of ferrous sulphate reduces the content of chromium dissolved in a cement-water mixture. The ferrous sulphate can, for example, be added during the preparation of mixtures containing cement or during the manufacture of the cement. Iron (II) sulphate reduces Cr^{6+} to Cr^{3+}, which has low solubility in the cement-water mixtures. Thus, the reaction between the Fe^{2+} and Cr^{6+} ions takes place in aqueous medium, i.e. when the water is added to the cement containing iron (II) sulphate.

Since the nineteen-seventies, cement manufacturers have been performing a ferrous sulphate treatment in particular at the time of the grinding step in order to reduce the chromium VI content in the cements and thus limit the risks of eczema being contracted by construction workers in regular contact with cement-water mixtures. However, this ferrous sulphate treatment of cements that makes it possible to reduce the chromium VI content of the treated cements turns out to be rather ineffective and presents numerous disadvantages.

As a matter of fact, it turns out to be necessary in practice to use iron sulphate in powder form in order to obtain reduction of chromium (VI) to chromium (III) with iron (II) ions. Now, oxygen in the air can convert iron (II) to iron (III). For this reason, particular attention as well as particular implementation conditions prove indispensable.

Other reduction pathways of chromium (VI) have been developed, as for example the reduction of chromium (VI) by organic systems such as aldehydes, and heterocyclic

compounds such as, for example, pyridine. But use of these organic systems in practice has proven maladapted for economic reasons connected in particular to the low stability of these organic systems in the preparations of cement or to the quantities to be used. It is known, moreover, in the state of the art that a solution of soluble Sn^{2+} ions makes it possible to reduce chromium VI.

There is, therefore, in the state of the art, no aqueous suspension with a base of tin hydroxide, and/or iron hydroxide and/or manganese hydroxide of pH between 2 and 11, limits excluded, capable of reducing the chromium VI content of cement, cumulatively fulfilling the following conditions:

- high stability, even in concentrated suspension,
- viscosity of the suspensions constant over time and which remains low,
- viscosity in concentrated solution sufficiently low so as to facilitate their use,
- formulation at a pH between 2 and 11, limits excluded, to facilitate storage, transport and conditions of implementation.

Surprisingly, it was found that an aqueous suspension of the hydroxide of at least one transition element and/or of tin, in particular of tin hydroxide and/or iron hydroxide and/or manganese hydroxide with a pH between 2 and 11, limits excluded, reduces the chromium VI content of the cement to a value at most equal to 2ppm and is characterised in that it comprises from 0.5 to 80% by weight of dry matter of the hydroxide of at least one transition element and/or of tin, in particular of tin hydroxide, and/or iron hydroxide and/or

manganese hydroxide with respect to the quantity of water, the hydroxide being implemented alone or as a mixture and in that it is stabilised by a hydrosoluble stabilisation agent.

ABSTRACT

The invention relates to a hydroxide aqueous suspension of at least one selected transition element and/or of tin of which the potential oxidation reduction is less than of the pair $CrO_4^{2-}/Cr(OH)_3$ (-0.12 V) having a pH between 2 and 11, limits excluded, for reducing the content of chrome VI of cement to a value no greater than 2 ppm. The suspension is characterized in that it contains 0.5 to 80% by wt. of dry material of hydroxide of at least one transition element and/or of tin with regard to the quantity of water and in that it is stabilized by a hydrosoluble stabilizer. This suspension makes it possible to reduce the content of chrome VI of cements to a value no greater than 2 ppm.

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CLAIMS

1. Aqueous suspension of the hydroxide of at least one selected transition element and/or of tin, whose oxidation-reduction potential is less than that of the CrO_4^{2-} / $Cr(OH)_3$ couple with a pH between 2 and 11, limits excluded, to reduce the chromium VI content of cement to a value at most equal to 2 ppm, characterised in that it includes from 0.5 to 80% by weight of dry matter of the hydroxide of at least one transition element and/or of tin with respect to the quantity of water and in that it is stabilised by a hydrosoluble stabilisation agent.

2. Aqueous suspension of the hydroxide of at least one transition element and/or of tin as claimed in claim 1, characterised in that it preferentially includes from 5 to 70% by weight of dry matter of the hydroxide of at least one transition element and/or of tin with respect to the quantity of water, and more preferentially from 10 to 60% by weight of dry matter of the hydroxide of at least one transition element and/or of tin with respect to the quantity of water.

3. Aqueous suspension of the hydroxide of at least one transition element and/or of tin as claimed in one or the other of claims 1 and 2, characterised in that the hydroxides of the transition elements and/or of tin are chosen from the group formed by iron hydroxide and manganese hydroxide, taken alone or in a mixture.

4. Aqueous suspension of the hydroxide of at least one transition element and/or of tin as claimed in any of the preceding claims, characterised in that the hydrosoluble stabilisation agent is a dispersing agent of molar mass less than 100,000 g/mol.

5. Aqueous suspension of the hydroxide of at least one transition element and/or of tin as claimed in claim 4, characterised in that the dispersing agent is chosen from the group made up by the polynaphthalene sulfonates, the polyoxyalkylene di-phosphonates and the polyoxyalkylene polycarboxylates.

6. Aqueous suspension of the hydroxide of at least one transition element and/or of tin as claimed in claim 5, characterised in that the dispersing agent is chosen from among the polynaphthalene sulfonates of molar mass less than 100,000 g/mol.

7. Aqueous suspension of the hydroxide of at least one transition element and/or of tin as claimed in claim 5, characterised in that the dispersing agent is chosen from among copolymers of the polycarboxylic type obtained by polymerisation of a polyalkyleneglycol monoester monomer containing from 2 to 300 molecules of oxyalkylene with at least one monomer chosen from among the unsaturated monocarboxylic acids and the unsaturated dicarboxylic acids.

8. Aqueous suspension of the hydroxide of at least one transition element and/or of tin as claimed in claim 7, characterised in that the dispersing agent is chosen from

among (meth)acrylate copolymers with a polyoxyalkylene polyalkylene glycol chain containing from 2 to 300 molecules of oxyalkylene.

9. Aqueous suspension of the hydroxide of at least one transition element and/or of tin as claimed in claim 5, characterised in that the dispersing agent is chosen from among the polyoxyalkylene di-phosphonates, and preferentially the polyoxyethylene di-phosphonates.

10. Aqueous suspension of the hydroxide of at least one transition element and/or of tin as claimed in claim 1, characterised in that it also includes an agent for adjusting the viscosity of said suspension.

11. Aqueous suspension of the hydroxide of at least one transition element and/or of tin as claimed in claim 10, characterised in that the agent for adjusting the viscosity is chosen from among hydrosoluble polymers of molar mass greater than 10^6 g/mol.

12. Aqueous suspension of the hydroxide of at least one transition element and/or of tin as claimed in claim 11, characterised in that the agent for adjusting the viscosity is chosen from the group made up by the xanthane, welan, carouba and guar gums, the celluloses and their derivatives.

13. Aqueous suspension of the hydroxide of at least one transition element and/or of tin as claimed in claim 11, characterised in that the agent for adjusting the viscosity is a hydrosoluble polymer of molar mass greater

than 10^6 g/mol chosen from among the polyethylenes, the polyacrylates and their derivatives.

14. Aqueous suspension of the hydroxide of at least one transition element and/or of tin as claimed in any of the preceding claims, characterised in that it presents a pH precisely between 2 and 11, limits excluded.

15. Use of aqueous suspensions of the hydroxide of at least one transition element and/or of tin of pH between 2 and 11, limits excluded, designed to reduce the chromium VI content of cement as claimed in claim 1 to produce cements whose chromium VI content is at most equal to 2 ppm.

16. Process for treatment of cements, characterised in that introduction is made, after the clinker calcination step during the cement preparation process the cement, of an aqueous suspension of the hydroxide of at least one transition element and/or of tin with a pH between 2 and 11, limits excluded, as defined in claim 1 to reduce the chromium VI content of the cements to a value at most equal to 2 ppm and produce cements whose chromium VI content is at most equal to 2 ppm.

17. Use of cement produced by the process for treatment of cements as claimed in claim 11 and whose chromium VI content is at most equal to 2 ppm to prepare a concrete composition comprising treated cement, water and the usual components.

18. Concrete compositions comprising cement, water and the usual components, characterised in that at the time of mixture of the various components, addition is made of an aqueous suspension of the hydroxide of at least one transition element and/or of tin, of pH between 2 and 11, limits excluded, as defined in claim 1, in sufficient quantity to reduce the soluble chromium VI content to a value at most equal to 2 ppm of Cr(VI).